

Synthesis, Characterization and Properties of Clay-Polyacrylate Hybrid Materials

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ABSTRACT: A new type of hybrid material of clay with poly (butyl acrylate) (PBA) has been prepared successfully using intercalation-polymerization process. The structure of the composite was investigated by X-ray diffraction (XRD), Fourier transform infrared (FTIR), Transmission electron microscope (TEM), and Thermogravimetric analysis (TGA). The results show that the hybrid material prepared has a decomposition central temperature of 485.6°C, 83°C higher than that of pure PBA (402.0°C). © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 796–801, 2000

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Organomineral derivatives are of interest because they combine the structural, physical and chemical properties of both inorganic host material and the organic guest species at a nanometer scale, for example polymer-silicate nanocomposites exhibit increased modulus,^{1–3} decreased thermal expansion coefficient,² reduced gas permeability,^{2,4} increased solvent resistance,⁵ and enhanced ionic conductivity⁶ when compared to the pristine polymers. These performance improvements, though, depend greatly on the distribution, arrangement, and interfacial bonding between the silicate layers and the polymer.⁷

Recently, many polymer-silicate composites have been reported, such as polypropylene/montmorillonite,^{4,8–10} nylon 6/montmorillonite (or hectorite, saponite and synthetic mica),¹¹ epoxy/magadite,¹² polystyrene/montmorillonite,¹³ epoxy/montmorillonite¹⁴ etc., but they applied silicates which were mainly montmorillonite and were purified with physical methods. In fact the nature of

silicate mineral is of a two or more silicate mixture, the unmodified natural silicates with polymers form hybrid materials which have more practical application. Seckin et al.¹⁵ have prepared successfully a new type of material incorporating bentonite (a mixture of kaolinite and montmorillonite) with an alkoxide using a sol-gel process, but bentonite and alkoxy vinylsilane formed covalent bonding between only the OH groups of the surface layer of the kaolinite phase in bentonite and the OH group of the silanols. The alkoxy vinylsilanes did not intercalate into the interlayer of the kaolinite phase in the bentonite.

In this paper, we successfully synthesized a polyacrylate/natural clay (mixture of kaolinite and muscovite) by diffusing butyl acrylate (BA) into the interlayer of modified clay, polymerizing, and then blending the polyacrylate/clay with polymers (such as polypropylene (PP), Yinzhong Polypropylene Chemical Ltd., Guangdong, P.R. China; polyethylene (PE), Oilu Petrochemical Ltd., Shandong, P.R. China; poly(vinyl chloride) (PVC), LG Chemical Ltd., Korea; and poly(styrene-butadiene-styrene) (SBS), Yueyang Petrochemical Ltd., P.R. China; etc.) to form compos-

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ites, for improving strength and toughness of the polymers. Here, we mainly discuss the structure, structure changes and thermal properties of the PBA/clay hybrid materials.

EXPERIMENTAL

Materials

The clay used in this study was from Yinhu, Guangdong. Purification was carried out by a sedimentation method and possible phases of the clay were examined by the XRD technique, diffraction peaks of the phases were determined by the fingerprint method. The chemical composition of the clay is 32.75% Si, 5.3% Al, 0.46% Fe, 0.35% Ca and 0.24% Mg, which was determined by atomic absorption spectrometry. Dimethyl sulfoxide (DMSO), glutamic acid (GA) and BA were commercially available.

Preparation of Clay-PBA Hybrid Materials

The preparation of clay-PBA hybrids was carried out via a three-step process. First 30 g clay and 100 ml DMSO were placed in a 250 ml vessel and stirred with a magnetic stirrer at 80°C for 24 h. The product was filtered and dried in vacuum at 50°C and crushed in a mortar, clay-DMSO composite being obtained. Then GA 6 g, 6 ml of concentrated hydrochloric acid and 100 ml water were added in a 250 ml vessel, heated to dissolve GA completely, then 30 g clay-DMSO and 100 ml water were added to the mixture, and stirred with a magnetic stirrer at 80°C for 12 h. The product was filtered, washed three times with 100 ml of hot water, freeze-dried, then dried in vacuum at 50°C, and crushed in a mortar. A clay-DMSO composite was obtained. Last, a 500 ml three-necked separable flask, coupled with a mechanical stirrer, was used as the reaction vessel. In this vessel, 30 g of clay-GA, 13.5 ml of BA, 0.1 g of benzoyl peroxide (BPO) and 150 ml of toluene were mixed and stirred at 30°C for 48 h, then a condensation condenser and nitrogen pipe were connected and the mixture was heated in an oil bath at 60°C for 1 h, 70°C for 1 h, 80°C for 3 h and 100°C for 3 h. At the end of reaction, the product was filtered, washed three times with toluene, dried in vacuum at 80°C and crushed in a mortar. Clay-PBA hybrid materials were obtained.

RESULTS AND DISCUSSION

X-Ray Characterization

Fig. 1(a), (b), (c) and (d) are the X-ray diffraction patterns of the clay, clay-DMSO, clay-GA and

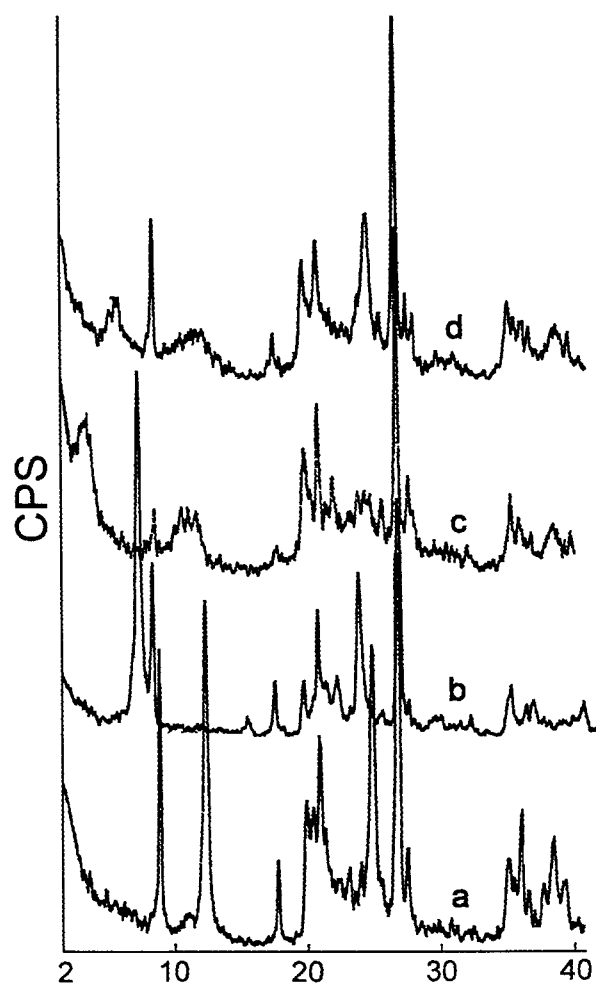


Figure 1 X-Ray diffraction patterns of (a) the clay, (b) the clay-DMSO, (c) the clay-GA and (d) the clay-PBA.

clay-PBA respectively. The results show that the peaks of 7.162, 4.350 and 3.579 Å of kaolinite disappear completely after reaction of clay with DMSO, and diffraction intensity of muscovite decreases. New peaks at 11.232, 3.994 Å are observed, and diffraction intensity of 11.232 Å is very strong. This result indicates that DMSO is intercalated into the interlayer space of clay and the clay-DMSO composite is formed. In addition, DMSO is mainly intercalated into the kaolinite phase of the clay.

Fig. 1(c) shows that the group peaks appear (25.545, 23.198 and 20.790 Å) and the peak at 11.232 Å of the clay-DMSO disappears, because DMSO in the interlayer of the clay is displaced by GA, the gallery height increases, forming the clay-GA composite.

With BA diffused and polymerized in the clay-GA composite, forming clay-PBA composite, the

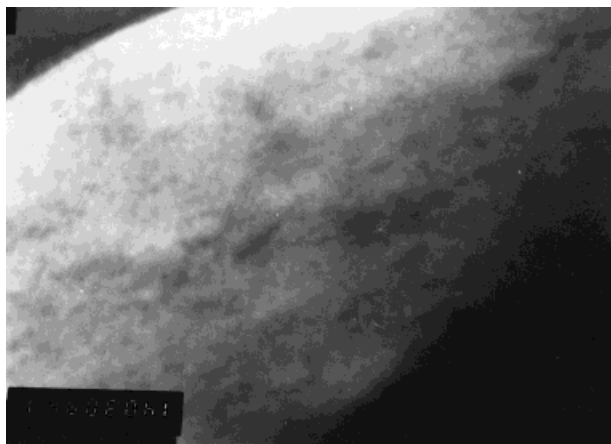


Figure 2 TEM image of PBA-clay nanocomposite (140000 \times).

peaks at 25.546, 23.198 and 20.790 \AA are replaced by 15.494 and 14.029 \AA ; in this case, the gallery heights of the clay decrease.

Why do the gallery heights of the clay-PBA decrease and the clay-GA and clay-PBA exist as multipeaks? We consider that the structure of GA contains two carboxyl groups ($-\text{COOH}$) and an amino-group (amino-acid), the hydrogen bond may form intermolecularly and a cross-linking

acrylamide may result during heating. Because the degrees of polymerization of the PBA are different, so the clay-GA and clay-PBA composites have multipeaks. Depending on the packing density, temperature and chain length, the chains are thought to lie either parallel to the host layers forming lateral mono- or bilayers or radiate away from the surface form in extended (paraffin-type) mono- or bimolecular arrangement.¹⁶ In some cases, individual chains are thought to adopt a hybrid arrangement with both lateral and paraffin-type segments leading to a pseudotrilayer. We consider that the chains of GA are thought to lie in a bi-molecular arrangement (paraffin-type) in the clay interlayer, but the chains of PBA are thought to lie in a mono-molecular arrangement (paraffin-type), so the gallery height of the clay-GA is higher than of the clay-PBA.

TEM Images

Fig. 2 is a TEM bright-field image of an organically modified layered silicate intercalated with BA diffusing and polymerizing. The dark lines are the cross sections of the 10 \AA thickness silicates layers. A face-face layer morphology is retained, but the layers are irregularly separated by $\sim 100\text{--}150$ \AA of PBA. The exfoliated result of the

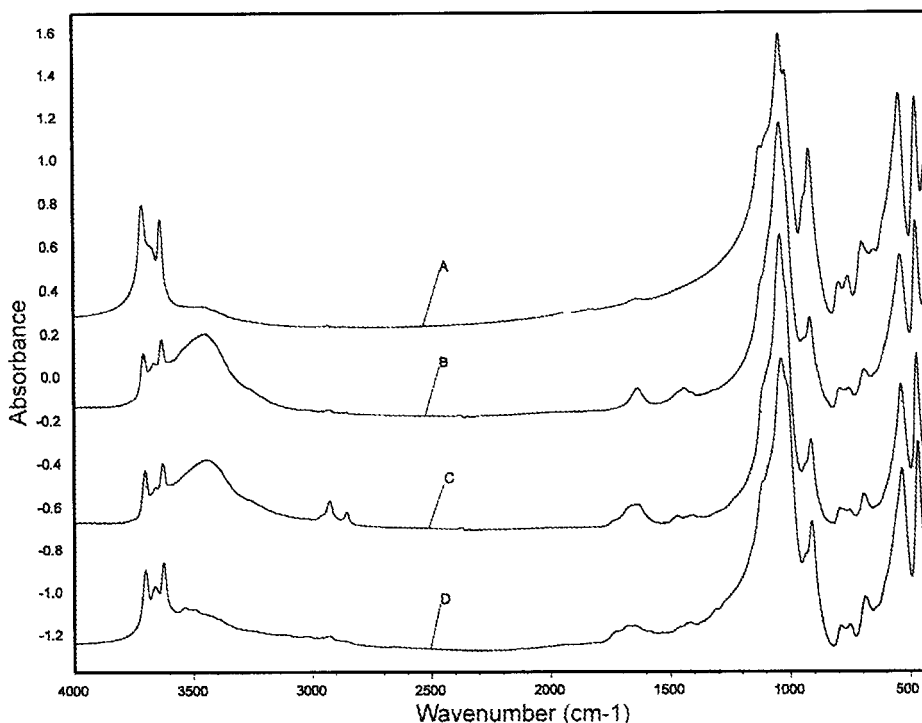
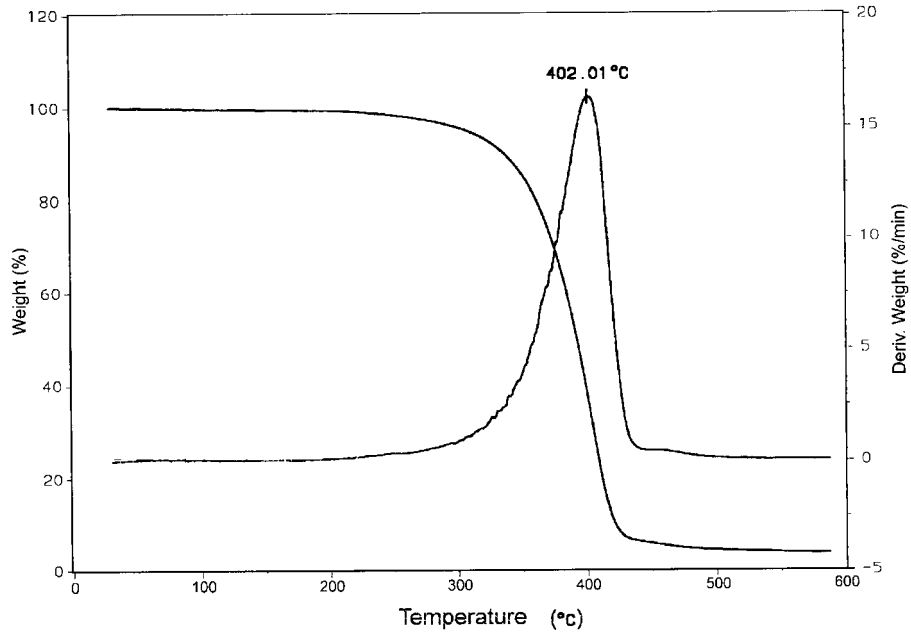
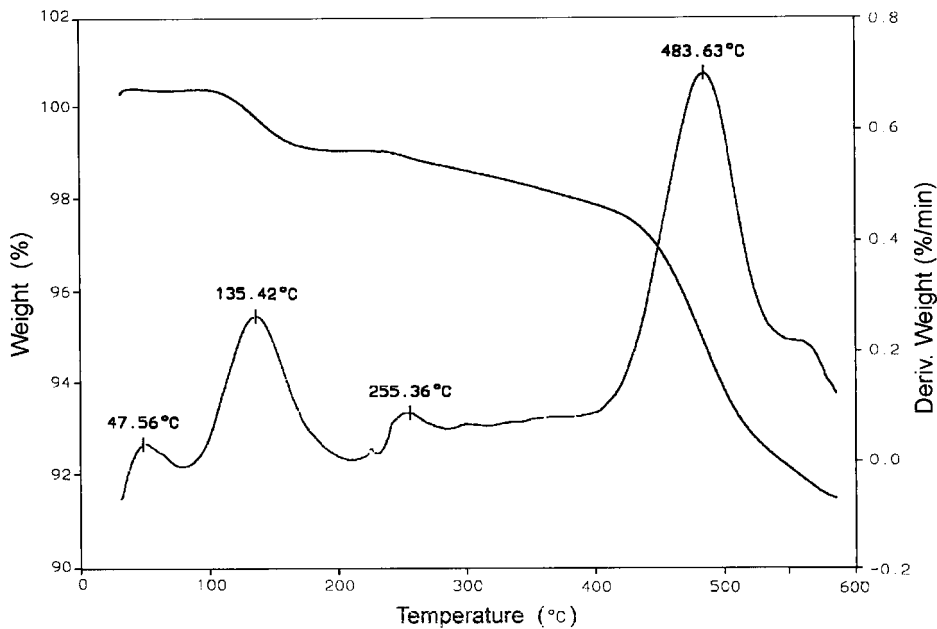


Figure 3 FTIR spectra of (a) the clay, (b) the clay-DMAO, the clay-GA and the clay-PBA.



(a) for pure PBA



(b) for the clay-PBA

Figure 4 TG curves.

clay interlayer is not very obvious in this photograph (TEM), because the clay is a mixture of kaolinite and muscovite, and the molecular

chains of the PBA or GA are not intercalated much into the muscovite phase of the clay. A similar phenomenon was obtained by K. Yano.²

FTIR Characterization

The IR absorption bands of layered silicates (including kaolinite and muscovite) at 3696, 3669, 3653 and 3621 cm^{-1} are attributed to O—H stretching vibrations, at 1117, 1033 and 910 cm^{-1} to Si—O stretching vibrations,^{17–20} the 3621 cm^{-1} is the O—H stretching vibrations band of the internal structure of layered silicates and 3696, 3669 and 3653 cm^{-1} bands are O—H stretching vibrations bands of interlayer surface of layered silicates. When the interlayer surface of layered silicates is modified, the 3621 cm^{-1} vibration band is not affected, while 3696, 3669 and 3653 cm^{-1} bands are affected.^{21–23} As clearly shown in Fig. 3, comparing IR spectra of the clay-DMSO, clay-GA and clay-PBA with the clay, the 3621 cm^{-1} vibration band remains unchanged, but the intensity of the 3696 cm^{-1} peak diminished, the 3669 cm^{-1} peak almost disappeared and the intensity of the 3653 cm^{-1} peak increased remarkably. In addition, it is noteworthy that no low energy bands, due to guest molecules hydrogen bonded to the interlayer hydroxyl groups, are observed in these cases. The absorption of the clay-DMSO at 3440 cm^{-1} and the absorption of the clay-GA at 3435 cm^{-1} come out as a broad peak, the clay-PBA absorption at 3533, 3492 cm^{-1} appeared as two weak peaks. These results show that the O—H of interlayer surface are disturbed because DMSO, GA and PBA are intercalated into the clay interlayer space. DMSO, GA and PBA intercalated into the clay interlayer space affect Si—O—Si lattice stretching vibration bands at 1117 and 1008 cm^{-1} too. The absorption bands of the clay-DMSO and clay-GA almost disappear and the intensity of the bands of the clay-PBA is clearly reduced.

Analyzing the IR spectra of the clay-DMSO, clay-GA and clay-PBA, it is also found that there are characteristic absorbed peaks of DMSO, GA and PBA respectively at 1437 cm^{-1} due to the —CH₃ stretching vibration absorbed peak, at 1470 cm^{-1} due to the N—H shear vibration absorbed peak, at 1638 cm^{-1} due to the C=O of GA stretching vibration absorbed peak, at 1726 cm^{-1} due to the C=O of PBA stretching vibration absorbed peak, and at 2930 and 2854 cm^{-1} due to the —CH₃, —CH₂, —CH symmetric and antisymmetric stretching vibration absorption peaks.

Thermal Analysis

TG curves for the pure PBA and clay-PBA are given in Fig. 4(a) and (b) respectively. The synthesis conditions of the pure PBA are the same as

the clay-PBA. As shown in Fig. 4(a), the decomposition temperature of the pure PBA in air is 212°C, the decomposition central temperature of that is 402°C, its weight loss degree reaches 98% at 550°C. In contrast, the thermal weight loss of the clay-PBA is in multisteps and some decomposition processes may be mutually overlapping.²⁴ Between 30 and 200°C, there are two thermal weight loss processes, the initial weight loss is 1.06%, this is due to a little volatile material and DMSO or GA small molecules adsorbed in the clay surface and in the clay interlayer space. Between 224 and 415°C, a 1.14% weight loss is observed, which is associated with a little PBA in the clay surface. A 6.75% mass loss is observed between 415 and 600°C, which is associated with PBA in the clay interlayer surface, its decomposition central temperature is 483.6°C. This indicates that the thermal stability of the clay-PBA is quite remarkable. Comparing the TG curves of the clay-PBA and pure PBA, we find that the decomposition temperature of PBA in the clay surface is same as the pure PBA, about 220°C. However, the decomposition temperature of the interlayer PBA is much higher than PBA out of the interlayer. The reasons may be that the specific area of clay interlayer surface is much larger than the outside surface and the PBA in the clay interlayer surface has a stronger interaction with the two-dimensional clay interlayer constraining the segmental motion of interlayer PBA. Besides, the clay interlayer has a shielding effect to external action (such as heat), making the interlayer PBA decrease in heat sensitivity. The decomposition central temperature of the clay interlayer PBA is 81.6°C higher than that of the pure PBA which is similar to Kojima's²⁵ report that the heat distortion temperature increased from 65°C for pure PA-6 to 160°C for PA-6 in a montmorillonite interlayer.

CONCLUSION

Using the replacing intercalation method, a kind of novel hybrid composite is prepared from the clay and PBA by modifying clay interlayer with DMSO first and then replacing it with GA, after which an acrylate monomer BA was diffused into the interlayer and then polymerized. XRD, TEM, FTIR and TG were used to characterize the structure, structure changes and thermal properties of the clay-PBA composite. The TG results indicate that the decomposition central temperature of the

clay-PBA increases about 80°C over that of the pure PBA.

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